Journal Name

ARTICLE

AIE phenomena of a cyanostilbene derivative as a probe of molecular assembly process

Fuyuki Ito,^{a*} Jun-ichi Fujimori,^a Narumi Oka,^a Michel Sliwa,^b Cyril Ruckebusch,^b Syoji Ito^c and Hiroshi Miyasaka^c

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Initial processes of the crystallization of a solute molecule, 1-cyano-trans-1,2-bis-(4'-methylbiphenyl)-ethylene (CN-MBE) in binary solutions (water and acetone), were investigated by means of fluorescence spectroscopy as well as scanning electron microscopy (SEM). With an increase in the volume fraction (V_w) of poor-solvent (water) in solutions, drastic change of the fluorescence of CN-MBE in spectra and intensity was observed. This change was attributed to the aggregation induced emission (AIE). By analyzing the evolution of AIE by multivariate curve resolution-alternating least squares (MCR-ALS), it was revealed that four main species appeared in solutions depending on V_w values. On the basis of the molecular exciton theory, we assigned these four emissive states to monomer, H-dimer, J-dimer, and H-aggregates, respectively. Interestingly, J-dimer state was observed only in the V_w range of 40% to 50%, just before the formation of the aggregate. This result suggests that the J-dimer takes an important role of the precursor in larger aggregates leading to the crystal formation. By integrating the present result with the previous one on the crystallization of CN-MBA through the solvent evaporation, we discussed the dynamics of the crystallization from the viewpoint of the sequence of molecular species appearing in the aggregation in solutions.

1. Introduction

Over the past decade, a number of investigations have been accumulated on aggregation-induced (or enhanced) emission (AIE or AIEE) in organic molecules.^{1–3} As reported by Tang et al.,⁴ even though the fluorescence quantum yield is low in solution, a series of silole derivatives in solid and/or aggregated states showed bright emission, due to the restriction of some geometrical motions in the solid/aggregated states inhibiting the rapid deactivation into the ground state.⁵ Since this report in 2001, a number of investigations have followed in the field of material chemistry on organic electroluminescent devices.^{6,7} Generally, fluorescent organic molecules such as a Rhodamine dyes exhibit the concentration quenching both in solution and in the solid state due to the aggregation-caused quenching. Therefore, AIE has been attracting much attention as a unique phenomenon of the fluorescence properties, leading to an improvement of organic luminescent materials.

The conversion of the fluorescent properties depending on aggregated states can also provide the information on the evolution of the aggregation processes.⁸ Molecules non-emissive in the solution suddenly turn into the highly emissive state owing to the aggregation and segregation. In addition, the temporal evolution of the emission can visualize series of complex interfacial assembling processes through the change of the color and intensity of the emission being strongly dependent on the property of the aggregation state. In comparison to conventional real-time imaging methods, AIE imaging technology is simple yet highly specific and sensitive, offering a clear view into the “interfacial world” including microemulsion, coffee-ring, and breath figure evolution, with ultralow background signal. In actual, the AIE imaging has been applied for the first time into the dynamic detection of the formation of breath figures and revealed its detailed mechanism through the analysis based on the theoretical modeling and simulation.⁸

Along this line, we have been applying the AIE imaging and the analysis of the spectra for the crystal formation process of the solute molecule during the evaporation of the solvent in solution phase.⁹ Spectroscopic evolution in organic fluorescent dyes during the solvent evaporation provide information on the sequences of molecular assembly, such as nucleation and growth of crystals^{10–12} by selectively observing the AIE properties.^{13,14} Recently, AIE was utilized in a fluorescence lifetime microscopy for the investigation of the nucleation and

^a Institute of Education, Shinshu University, Nagano 380-8544, Japan. E-mail: fito@shinshu-u.ac.jp; Fax: +81-26-238-4114; Tel: +81-26-238-4114

^b LASIR, UMR 8516, CNRS, Université des Sciences et Technologies de Lille, 59 655 Villeneuve d'Ascq Cedex, France.

^c Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: fluorescence lifetime data. See DOI: 10.1039/x0xx00000x

growth of the AIE molecule during a precipitation in a micro-flow.¹⁵

In previous papers¹³, we reported the aggregation behaviours of a cyanostilbene derivative [1-cyano-trans-1,2-bis-(4'-methylbiphenyl)-ethylene (CN-MBE)] for the AIE, as one of the typical systems^{16,17} as revealed by the fluorescence microscope images and emission spectra in a 1,2-dichloroethane droplet. During solvent evaporation, CN-MBE fluorescence intensity was increased and spectral shape gradually evolved in time. The analysis of the time evolution of the emission spectra revealed that the spectral evolution was due to the population change of the two species, the planer monomer and J-aggregates, and the fluorescence from J-aggregates was established prior to the increase in total intensity. These results strongly suggested that J-aggregates play an important role as precursors in the formation of crystal nuclei, and the growth from J-aggregates to the crystal nuclei is the rate-determining step in the nucleation process.¹³

The solvent evaporation process, however, complicates the extraction of detailed information on the structure of molecular packing and their sizes because the evolution of the solvent evaporation is a dynamic process. Although the importance of the J-Aggregates was pointed out, the detailed mechanism such as nuclei formation in the AIE molecules and the structure of the aggregated states have not yet elucidated. So as to elucidate the molecular packing and aggregated states in the present work, we have investigated molecular dynamics of initial stage of crystal formation by detecting the temporal evolution of the spectrum and intensity of an AIE in nanoparticle solutions as a function of volume fraction (V_w) of poor-solvent (water) in the re-precipitated liquid, the method of which has been developed by Nakanishi and Kasai group.^{18, 19} By applying multivariate curve resolution-alternating least squares (MCR-ALS)²⁰⁻²² was applied for the analysis of the fluorescence excitation spectra in order to extract of the abundance profiles and spectra of the individual species and aggregates.

2. Experimental

2.1 Materials

CN-MBE was synthesized according to a previous paper.¹⁶ Ultrapure water treated by a purifier (Mill-Q, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) and acetone (Wako, spectral grade) were used. The nanoaggregates were prepared according to the following procedure. Ultrapure water (Mill-Q, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used as a dispersion medium. An acetone solution of CN-MBE ($2.0 \times 10^{-4} \text{ mol dm}^{-3}$) was rapidly injected into vigorously stirred (1500 rpm) ultrapure water (0 to 4.5 mL) prepared by the purifier (Mill-Q, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) at ambient temperature. The concentration of the CN-MBE nanoaggregates thus obtained was $2.0 \times 10^{-5} \text{ mol dm}^{-3}$.

Samples for scanning electron microscopy (SEM) observation were prepared by dropping nanoaggregates solution containing 1 wt% polyvinyl alcohol (PVA) on a silicon wafer

previously treated with piranha solution. PVA was added to prevent aggregation during solvent evaporation on the wafer.

2.2 Measurements

A fluorometer (Shimadzu RF-5300PC) was used for the measurement of fluorescence spectra. Fluorescence lifetimes were measured with a time-correlated single-photon-counting system using an experimental setup.²³ The excitation light source was the second harmonic (355 nm) of a Ti:Sapphire laser (Spectra Physics, Tsunami). Fluorescence time profiles were analyzed by non-linear least-squares fitting with deconvolution of the actual instrumental response function (IRF). The typical time resolution by this method is ca. 5–10 ps. SEM images were acquired on a JSM-7000F (JEOL) microscope using a voltage of 10 kV.

2.3 Multivariate Curve Resolution–Alternating Least-Squares (MCR-ALS)

A brief description of the main steps of MCR-ALS applied to spectrophotometric data is given in the following. More comprehensive information can be found in the literature where the potential of this method in equilibrium studies has been reported.^{21, 24, 25} The aim of MCR-ALS is to decompose a data matrix **D** containing spectra of a unknown chemical mixture into two matrices, **C** and **S^T**, containing respectively pure concentration profiles and pure spectra of the different species composing the unknown mixture. This can be achieved according to the following equation.

$$\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$$

In this equation, the matrix **D** ($m \times n$) contains m dependent fluorescence excitation spectra (rows) registered at n wavelength (columns) and the matrices **C** ($m \times N$) and **S^T** ($N \times n$) contain the dependent abundance profiles and the characteristic spectra of the N emissive species observed in the mixture, respectively. The matrix **E** ($m \times n$) contains the residual signal, which is mostly due to experimental noise. In spectroscopy, the model in the equation above provide simplified and interpretable information of the process data, under the premise that the multicomponent Beer's law is valid. This model can be extended to the simultaneous analysis of multiple experiments (multi-set) for which the equation above would remain valid. In this way, a more reliable and accurate description of the chemical system is usually provided.

3. Results and Discussion

3.1 Fluorescence properties of CN-MBE

Fig. 1 shows the fluorescence spectra of CN-MBE in acetone/water mixtures with different volume fractions (V_w) of water. While the fluorescence intensity is very low in the range of $V_w < 40\%$, it drastically increases with an increase in V_w in the range of $V_w > 45\%$. This drastic increase is due to the AIE¹⁶ as a synergistic effect of intermolecular planarization and aggregation of nanoparticles.

To more clearly elucidate the evolution as a function of V_w , fluorescence spectra were normalized in Fig. 1b. For $V_w < 40\%$,

the fluorescence maximum located at 430 nm. At $V_w = 40\%$, the broad spectrum shifted into the red region with a maximum at 450 nm with two shoulders at 430 and 480 nm. In the region of $V_w > 40\%$, the drastic change of the fluorescence band shape was observed: its peak was around 480 nm with a shoulder at 440 nm. These spectral changes can be interpreted in the following way. The weak fluorescence in the range of $V_w < 40\%$ is due to the monomer in the environment where the torsion can induce the nonradiative deactivation in the non-aggregated state.²⁶ With increasing V_w , colloidal aggregates were formed by reprecipitation. The fluorescence peak shift can be ascribed to the elongation of the π -conjugation caused by the planarization resulting from the coaggregation. Recent theoretical investigation by Sekiya et al.²⁷ supports that a peak at 460 nm and shoulder at 420 nm in the fluorescence spectra could be assigned to the twisted and (near) planar structures of CN-MBE. On the other hand, the fluorescence spectrum around $V_w = 40\%$ is different from these two species and could be attributed to the transient species between the monomer and aggregated states.

As the size of the aggregates increases with increasing V_w , their fluorescence intensity was enhanced by AIE. Crystallization accompanying the planarization of the molecule has been confirmed by X-ray structure analysis of other cyanostilbene derivatives.^{26, 28, 29} These findings indicate that AIE of CN-MBE occurred after molecular planarization.

Fig. 1 (a) Fluorescence spectra of CN-MBE in acetone/water mixtures with different water contents and (b) spectra normalized at the maximum intensity.

Fig. 2 Fluorescence time profiles of CN-MBE in acetone/water mixtures with different water contents monitored at (a) 430 nm and (b) 470 nm following excitation at 355 nm.

3.2 Fluorescence lifetime of CN-MBE

Fig. 2 shows the fluorescence decay profiles of CN-MBE in acetone/water mixtures as a function of V_w monitored at 430 and 470 nm following excitation at 355 nm. The fluorescence decay curves for all of different V_w conditions were well reproduced by triple exponential functions, as listed in Table S1. Typical time constants were 20–520 ps, 1–2 ns, and 2–5 ns (see details in Table S1). The amplitude of the component with a lifetime $\tau < 10$ ps was larger than 98% for $V_w < 40\%$. This short lifetime is due to the rapid nonradiative process through the twisted structure. The components with $\tau \sim 1$ –2 ns and 2–5 ns are most probably originated from the planar monomer and elongation of the lifetime due to the CN-MBE aggregation formation, respectively. No remarkable difference was observed for the time profiles in the monitoring wavelength range of 430–470 nm, indicating that the time profile monitored at 430 nm involves the contribution of the species whose emission maximum locates at 470 nm.

To more precisely elucidate this evolution, we measured the fluorescence excitation spectra for the fluorescence at 490 nm (Fig. 3). Only one peak around 360 nm was observed for $V_w = 0\%$ to 30%. In addition to this maximum, a shoulder around 420 nm appeared at $V_w = 40\%$. New peaks appeared around both 340 and 400 nm when $V_w = 45\%$. For V_w from 50% to 55%, broad spectra were observed. For $V_w > 60\%$, the excitation spectra were blue-shifted and the intensity around

420 nm decreased with further increase in Vw. Generally, fluorescence excitation spectra reflect ground-state absorption spectra. Dependence of the excitation spectra on Vw indicates that the molecular forms of CN-MBE in the ground state is dependent on Vw.

Fig. 3 Dependence of fluorescence excitation spectra of CN-MBE monitored at 490 nm in acetone/water mixtures on water content.

Amplitudes of the three time constants mean fluorescence lifetime $\langle\tau\rangle$ monitored at 470 nm are plotted as a function of Vw together with the fluorescence peak wavelength and integrated fluorescence intensity obtained from steady-state fluorescence spectra in Fig. 4. The $\langle\tau\rangle$ values were obtained from $\langle\tau\rangle = \sum A_i \tau_i / \sum A_i$, where A_i is the amplitude of the pre-exponential factor for i th component of τ , because the behavior of the τ value of each component is complicated. The A_1 component with $\tau \sim 20$ –520 ps decreased when $Vw > 40\%$ concomitant with the increase of the A_2 component with $\tau \sim 1$ –2 ns. The A_3 component with $\tau \sim 2$ –5 ns increased steeply with rising Vw. Meanwhile, $\langle\tau\rangle$ displayed stepwise increases at $Vw = 40\%$ and 60% . These findings suggest that the elongation of the fluorescence lifetime originates from the aggregate formation with increasing Vw.

Fig. 4 Water fraction (Vw) dependence of the maximum fluorescence intensity and peak wavelength, and relative amplitude and mean fluorescence lifetime of CN-MBE in acetone/water solution.

3.4 Multivariate resolution of water fraction-dependent fluorescence excitation spectra

The fluorescence excitation spectra of CN-MBE are strongly dependent on Vw. To unveil this spectral evolution and elucidate the structure on molecular packings MCR-ALS was applied to the fluorescence excitation spectra. Fig. 5a and b present the four forms obtained by multi-set MCR-ALS analysis and profiles of the relative abundance of the four species as a function of Vw at each monitoring wavelength, respectively. The colours of circles indicate those of the corresponding spectra. The abundance of the blue spectra monotonically decreases with increasing Vw and finally reached zero in the region of $Vw > 50\%$. The portion of the green spectrum is 20 % for $Vw < 50\%$. The abundance of red spectra steeply increased with Vw, and eventually became the major component of the nanoaggregate. The orange spectrum only existed for Vw in the range of 40% to 50%. The evolution of the relative abundance of the four species as a function of Vw was well reproduced at all monitoring wavelengths.

The changes of the excitation spectra with Vw can be interpreted by Kasha's theory.^{30–32} Through the dipole–dipole interaction in the aggregate, one energy level of the excited state in the monomer splits into two levels with different energies. Spectroscopic characteristics of the dimer depend on the morphology of the dimer. In H-aggregates, two molecules are aligned in parallel (sandwich-like structure) or coplanar displaced with an angle $\theta > 54.7^\circ$. The optical transition to the higher excited state is allowed in the absorption, and deactivation to the ground state is via the lowest excited state. Accordingly, formation of H-dimers is characterized by blue-

shifted absorption bands with respect to those of the monomer. In contrast, molecules in J-aggregates are arranged in head-to-tail direction or coplanar displaced with $\theta < 54.7^\circ$. The transition to the lowest excited state is allowed in the optical absorption. J-aggregates are characterized by a red-shifted absorption maximum compared to that of the monomer.

According to the Kasha's exciton interaction theory, the present evolution of CN-MBE could be interpreted in the following manner. CN-MBE existing in the monomer state at low V_w turns into the J-aggregate with increasing V_w . With further increase in V_w , it altered to the H-aggregate. The blue, green, red and orange spectra could be respectively assigned to monomer, H-dimer, H-aggregate, and J-dimer. As was shown in Fig. 3, we could distinguish two species, dimers (composed of two molecules) and aggregates (composed of three or more molecules).

Interestingly, the J-dimer state was observed only in the V_w range of 40% to 50%, corresponding to the region where fluorescence enhancement was observed (Fig. 4). The appearance of the J-dimer was observed just before the formation of the aggregate also in the previous study on the solvent evaporation-induced crystallization of CN-MBE.¹³ These results strongly suggest that the J-dimer takes an important role as a transient species for the formation of the aggregates.

Fig. 5 (a) Fluorescence excitation spectra of CN-MBE and (b) V_w -dependent profiles of four states of CN-MBE molecular arrangements obtained by MCR-ALS analysis.

3.5 SEM images of CN-MBE nanoparticles

To directly obtain the information on the structure of aggregates, we measured SEM images of CN-MBE in acetone/water mixtures with different V_w after drying the solution with PVA on the substrates (Fig. 6). In the mixtures with $V_w < 45\%$, no aggregates was observed in SEM images. As shown in Fig. 5a, unclear and irregularly shaped aggregates were observed at $V_w = 50\%$. Clear image of particles was

observed in the range of $V_w \geq 60\%$. Sharp nanoparticles with a width of ca. 300 nm were observed at $V_w = 90\%$. These images clearly indicate that the aggregation and formation of nanoparticles of CN-MBE with increasing V_w lead to the fluorescence spectral changes.

Fig. 6 SEM images of CN-MBE aggregates in acetone/water mixtures with water contents of (a) 50%, (b) 60%, (c) 65%, and (d) 90%.

3.6 Fluorescence evolution during the molecular assembling process

From the results so far, we summarize the fluorescence evolution during the molecular assembling processes of CN-MBE in Fig. 7. The H- and J-dimers have different geometrical arrangements of the monomer. According to Kasha's exciton model, the emitting state in the H-dimer is dipole-forbidden (or less allowed), whereas that of the J-dimer is allowed.^{30, 31} Much larger exciton splitting can take place in larger aggregates than in the dimer. That is, the higher energy state shifts to much higher in energy and lower energy one shift to much lower with increasing size of the aggregates.³² Accordingly, the band of the H-aggregate could be blue-shifted and that of the J-aggregate could be red-shifted compared with the band of the monomer, as schematically illustrated in Fig. 7. The simulated spectra from MCR-ALS (orange line in Fig. 5a) show absorption bands both in longer and shorter wavelength regions. The coexistence of the two bands may be due to the oblique arrangement (spatial symmetry breaking of the dimer) of CN-MBE molecules in the aggregates. That is, not perfectly aligned in parallel or perpendicular for the two molecules may lead to the partial appearance of the forbidden transitions.

Fig. 7 Schematic representation of the exciton coupling in the molecular aggregates.

Also for the emission, the signal from the H-dimer was detected as the fluorescence excitation spectra, although the emission from the H-dimer is a forbidden transition in the framework of Kasha's theory. On the AIE of CN-MBE, Gierschner and Park reported that the aggregates of CN-MBE tend to take J-aggregation with enhanced fluorescence emission instead of H-aggregation in the solid state,^{33, 34} owing to the bulky polar cyano group in CN-MBE playing an important role in the restriction of the parallel face-to-face intermolecular conformation. By integrating these studies^{33, 34} with the present results, it is strongly suggested that the enhanced emission of CN-MBE is due to the combined effects of aggregation-induced planarization and J-aggregate formation. As was shown in Fig. 5, the fluorescence excitation spectra indicated the contribution from the H-aggregates. This contribution suggests several mechanisms; (i) energy transfer from the H-dimer to the J-dimer acting as a trap site, (ii) a low exciton trapping probability in the uniform crystal structure induced by tight stacking of cyanostilbene motifs¹⁷ and (iii) weak coupling caused by molecular distortion such as oblique aggregation leading to the transition partially allowed from the lower energy site. In addition, Matsuda et al.³⁵ reported, on the basis of the temperature dependence and DFT calculation, that the AIE effects of CN-MBE could be attributed to H-aggregates enhancing the excimer emission. In anyhow, the emission from the H-aggregates is still under the vivid investigation.

Fig. 8 Schematic representation of the aggregation process of CN-MBE in acetone/water mixtures.

Fig. 8 shows a schematic representation of the aggregation process of CN-MBE in acetone/water mixtures based on the V_w dependence of the fluorescence excitation spectral changes and MCR-ALS analysis. At $V_w < 40\%$, monomer, H-dimer and H-aggregates co-exist in the solution and the

fluorescence intensity was quite low. With increasing Vw, the J-dimer is produced and small cluster of two monomers via intermolecular interactions or from the H-dimer by slip stacking. This small cluster is unstable because of its unfavorable surface free energy and dissociates before crystal formation. The abundance of J-dimers indicates the formation of subcritical clusters. In general, the nucleus formation rate, J , is given by the Arrhenius reaction rate equation: $J = A \exp(-\Delta G/k_B T)$, where k_B is Boltzmann's constant, A is the pre-exponential factor, and ΔG is the Gibbs energy of cluster formation³⁶ Because of the energy barrier, critical nuclei formation is in competition with the dissolution. Accordingly, the difference of Vw dependencies between J-dimer abundance and the total fluorescence intensity may be related to this process for the growth to the crystal nuclei from J-dimers acting as the rate-determining step. That is, the formation of the J-dimer leads to the larger aggregates.

4. Conclusions

We employed emission spectroscopy to elucidate the molecular dynamics of the initial stage of crystal formation of CN-MBE in binary solution (water and acetone). Emission spectrum and intensity of the solute, CN-MBE, were strongly dependent on the volume fraction (Vw) of water (poor-solvent) in solutions, which were attributed to AIE. The emission properties of main four species deduced from MCR-ALS analysis were discussed on the basis of Kasha's molecular exciton theory so as to derive the information on the structure of the aggregate. Interestingly, J-dimer state was observed only in the Vw range of 40% to 50%, just before the formation of the aggregate. This result suggested that the J-dimer took an important role as the precursor in larger aggregates leading to the crystal formation. The present results demonstrated that the detailed observation and analysis of AIE can provide the information on the dynamics of the molecular aggregation in the initial stage of crystal formation.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP26410009, JP26107002, JP15H01081 in Scientific Research on Innovative Areas "Photosynergetics". F.I and M.S. were also supported by CNRS-JSPS (SAKURA program, JSPS Campus France). C.R. and M.S acknowledge the financial support of the Agence National de la Recherche (ANR-14-CE08-0015-01 Ultrafast Nanoscopy).

Notes and references

- 1 B. Z. Tang and A. Qin, *Aggregation-Induced Emission: Fundamentals*, John Wiley & Sons, Inc., United Kingdom, 2013.
- 2 Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332-4353.
- 3 Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, 40, 5361-5388.
- 4 J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740-1741.
- 5 J. Q. Shi, N. Chang, C. H. Li, J. Mei, C. M. Deng, X. L. Luo, Z. P. Liu, Z. S. Bo, Y. Q. Dong and B. Z. Tang, *Chem. Commun.*, 2012, 48, 10675-10677.
- 6 J. Zhou, Z. F. Chang, Y. B. Jiang, B. R. He, M. Du, P. Lu, Y. N. Hong, H. S. Kwok, A. J. Qin, H. Y. Qiu, Z. J. Zhao and B. Z. Tang, *Chem. Commun.*, 2013, 49, 2491-2493.
- 7 H. Tong, Y. Q. Dong, Y. N. Hong, M. Haussler, J. W. Y. Lam, H. H. Y. Sung, X. M. Yu, J. X. Sun, I. D. Williams, H. S. Kwok and B. Z. Tang, *J. Phys. Chem. C*, 2007, 111, 2287-2294.
- 8 J. W. Li, Y. Li, C. Y. K. Chan, R. T. K. Kwok, H. K. Li, P. Zrazhevskiy, X. H. Gao, J. Z. Sun, A. J. Qin and B. Z. Tang, *Angew. Chem. Int. Ed.*, 2014, 53, 13518-13522.
- 9 F. Ito, Y. Suzuki, J. Fujimori, T. Sagawa, M. Hara, T. Seki, R. Yasukuni and M. L. de la Chapelle, *Sci Rep*, 2016, 6, 22918.
- 10 F. Ito, H. Sato, Y. Ugachi, N. Oka, S. Ito and H. Miyasaka, *Photochem. Photobiol. Sci.*, 2015, 14, 1896-1902.
- 11 F. Ito, Y. Kogasaka and K. Yamamoto, *J. Phys. Chem. B*, 2013, 117, 3675-3681.
- 12 F. Ito, Y. Ugachi and T. Sasaki, *Chem. Lett.*, 2012, 41, 282-283.
- 13 F. Ito and J.-i. Fujimori, *CrystEngComm*, 2014, 16, 9779-9782.
- 14 J. Fujimori, A. Katsuki and F. Ito, *Chem. Lett.*, 2016, 45, 421-423.
- 15 V. L. Tran, V. Genot, J. F. Audibert, Y. Prokazon, E. Turbin, W. Zuschatter, H. J. Kim, J. Jung, S. Y. Park and R. B. Pansu, *New J. Chem.*, 2016, 40, 4601-4605.
- 16 B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, 124, 14410-14415.
- 17 B. K. An, J. Gierschner and S. Y. Park, *Acc. Chem. Res.*, 2012, 45, 544-554.
- 18 H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh and H. Nakanishi, *Jpn. J. Appl. Phys. Part 2 - Lett.*, 1992, 31, L1132-L1134.
- 19 H. Kasai, H. Kamatani, Y. Yoshikawa, S. Okada, H. Oikawa, A. Watanabe, O. Itoh and H. Nakanishi, *Chem. Lett.*, 1997, 1181-1182.
- 20 H. Abdollahi and V. Mahdavi, *Langmuir*, 2007, 23, 2362-2368.
- 21 M. Rebarz, B. M. Kukovec, O. V. Maltsev, C. Ruckebusch, L. Hintermann, P. Naumov and M. Sliwa, *Chemical Science*, 2013, 4, 3803-3809.
- 22 C. Ruckebusch, M. Sliwa, P. Pernot, A. de Juan and R. Tauler, *J. Photochem. Photobiol. C*, 2012, 13, 1-27.
- 23 Y. Nagasawa, T. Itoh, M. Yasuda, Y. Ishibashi, S. Ito and H. Miyasaka, *J. Phys. Chem. B*, 2008, 112, 15758-15765.
- 24 R. Tauler, *Chemometrics and Intelligent Laboratory Systems*, 1995, 30, 133-146.
- 25 C. Ruckebusch and L. Blanchet, *Anal. Chim. Acta*, 2013, 765, 28-36.
- 26 C. W. Chang, C. J. Bhongale, C. S. Lee, W. K. Huang, C. S. Hsu and E. W. G. Diau, *J. Phys. Chem. C*, 2012, 116, 15146-15154.
- 27 Y. Fujimoto, N. Yamamoto, K. Furukawa and H. Sekiya, *Chem. Lett.*, 2016, 45, 637-639.
- 28 S. J. Yoon and S. Park, *J. Mater. Chem.*, 2011, 21, 8338-8346.
- 29 S. J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2010, 132, 13675-13683.
- 30 M. Kasha, H. R. Rawls and M. Ashraf El-Bayoumi, *Pure Appl. Chem.*, 1965, 11, 371.
- 31 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
- 32 M. Kasha, *Radiat. Res.*, 1963, 20, 51-71.

- 33 J. Gierschner, L. Luer, B. Milian-Medina, D. Oelkrug and H. J. Egelhaaf, *Journal of Physical Chemistry Letters*, 2013, **4**, 2686-2697.
- 34 J. Gierschner and S. Y. Park, *J. Mater. Chem. C*, 2013, **1**, 5818-5832.
- 35 T. Hirose, Y. Tsunoi, Y. Fujimori and K. Matsuda, *Chem. Eur. J.*, 2015, **21**, 1637-1644.
- 36 R. J. Davey, S. L. M. Schroeder and J. H. ter Horst, *Angew. Chem. Int. Ed.*, 2013, **52**, 2166-2179.